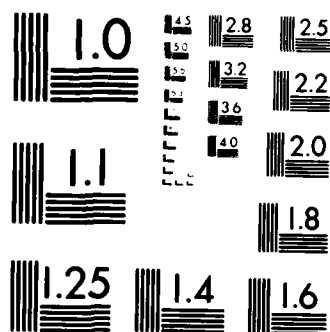AD-A150 469   OBSERVATION OF SURFACE VIBRATIONAL RESONANCES ON (110)   1/1
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Observation of Surface Vibrational Resonances on (110) Surfaces of FCC Metals.

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Inelastic dipole scattering of electrons from surface vibrational resonances of clean Cu(110) and Ni(110) surfaces has been observed. The resonances are shown by surface lattice dynamics calculations to be a characteristic signature of the (110) surface of fcc metals. The calculated spectral energies and shapes are in excellent agreement with experiments and shows that there are no significant changes in the surface force constants from the bulk values.

Vibrational spectroscopy of surface vibrational modes on clean and adsorbate covered metal surfaces is a viable method for obtaining valuable knowledge about the structure and the interatomic forces at the surface. [1,2] For a few close packed surfaces it has recently been possible by electron-energy-loss spectroscopy (EELS) [3] and inelastic He scattering [4] to observe surface phonon dispersion relations , modes attributed to surface resonances [5] and dipole excited bulk modes. [6] In this paper we present observations by EELS of dipole active surface resonances on the (110) surfaces of Cu and Ni. Calculations using surface lattice dynamics are in excellent agreement with measured spectra and show that these resonances have their physical origin in the *geometrical structure* of the (110) surfaces of face centered cubic crystals. In particular it is found that there are no significant changes in the surface force constants from the bulk values.

The EEL spectra were recorded in a multitechnique ultrahigh vacuum system with a base pressure of 4×10^{-11} Torr. [7] The EEL spectrometer consists of a monochromator and analyzer of the double pass 127° cylindrical electrostatic deflector type. The spectra were recorded in the specular direction with an incident angle of 60° with respect to the crystal normal. The scattering plane containing the incident and scattered electrons is defined by the surface normal and the $[1\bar{1}0]$ crystal direction. The angular acceptance of the analyzer is 1.8° at full-width-half-maximum (FWHM). Impact energies of 3.2 and 4.3 eV were used for Cu and Ni, respectively. Sample cleaning and characterization were done by standard procedures. [7]

The recorded spectra in Fig.1 display sharp spectral features which are only slightly broader than the elastic peak. The observed losses show the expected reduction in intensity from the Bose-Einstein factor on the gain side. Off specular measurements show that the inelastic scattering cross section follows closely those

of dipole active modes. The loss peaks occur at energies 20 and 24 meV, which scale with and lie well below the maximum bulk phonon energies at 30 [8] and 37 meV [9] for Cu and Ni, respectively. This fact suggests that these vibrational features are derived from the bulk phonons of the crystals. The electric field from the scattering electron can also excite electron hole pairs. [10] In general this mechanism gives rise to an additive contribution to the spectrum which decreases monotonically with frequency and accordingly can not be responsible for the observed sharp loss features.

The inelastic dipole scattering from phonons at metal surfaces is readily related to surface lattice dynamics of dipole active displacements. The lattice dynamics can be done analytically by a transfer matrix technique for a semi-infinite surface. [11]

The probability distribution $P(\vec{k},\vec{k}')$ for an electron with incident wavevector $\vec{k}$ to be detected in the direction $\vec{k}'$ with an energy loss $\hbar\omega$ and for small momentum transfers $\hbar\vec{q}_{\parallel} = \hbar\vec{k}_{\parallel} - \hbar\vec{k}_{\parallel}'$ parallel to the surface is given by [1,12]

$$P(\vec{k},\vec{k}') = \frac{2}{\hbar\pi(ea_0)^2\cos\alpha} \frac{k'}{k} \frac{q_{\parallel}^2}{(q_{\parallel}^2 + q_z^2)^2} S(\vec{q}_{\parallel},\omega) \qquad (1)$$

where α is the angle of incidence, a_0 the Bohr radius, $\hat{z}$ the surface normal and $q_z = |k_z + k_z'|$. The prefactor, i.e. the dipole matrix element, to the spectral function $S(\vec{q}_{\parallel},\omega)$ in Eq.(1) is sharply peaked close to $\vec{q}_{\parallel} = 0$. In this limit the spectral function is given by a temporal Fourier transform of a correlation function for the normal component of the dipole moment μ of the charge fluctuations in the metal.

For the high symmetry surfaces only a rigid displacement u_l of a layer l normal to the surface can give rise to a dipole moment μ. This means that the incident electron will essentially excite only longitudinal phonons propagating

along the direction normal to the surface by dipole scattering for the (110), (111) and (100) surfaces of Cu and Ni.

The effective charge e_l^* relates the dipole moment μ to the displacements u_l of the substrate layers through $\mu = \sum_l e_l^* u_l$. Recently it has been shown that the incomplete screening by the conduction electrons in the surface region can give rise to sufficiently large e_l^* so that the dipole coupling to the bulk phonons of the (100) surfaces of Cu and Ni is observable. [6] Here the same model is used for the effective charges where $e_1^* = -e_2^* = e^*$ and $e_l^* = 0$ for $l \geq 3$. Note that the sum of the effective charges has to be zero since a rigid translation of the whole crystal normal to the surface does not change the dipole moment.

In the harmonic approximation the spectral function $S(\overline{q}_\| = 0, \omega)$ can be directly related to a phonon density of states $g(\omega, \{n_l^*\})$ projected onto a normalized effective charge field $n_l^* = e_l^*/e_{tot}^*$ through [12]

$$S(\overline{q}_\| = 0, \omega) = \frac{(1 + n(\omega))}{a} \frac{e_{tot}^{*2} \hbar}{2M\omega} g(\omega, \{n_l^*\}) . \tag{2}$$

Here M is the mass of a substrate atom, $n(\omega)$ the Bose-Einstein distribution factor, a the area of the surface primitive cell and e_{tot}^* the modulus of the effective charge field $\{e_l^*\}$, i.e. in the adopted model $e_{tot}^* = \sqrt{2} e^*$, and

$$g(\omega, \{n_l^*\}) = \sum_\kappa | \sum_l n_l^* u_{\kappa l} |^2 \delta(\omega - \omega_\kappa) , \tag{3}$$

where $u_{\kappa l}$ is the rigid displacement of a substrate layer l for an eigenmode κ with energy $\hbar\omega_\kappa$ of the dynamical matrix $\overline{D}$.

A prerequisite for a meaningful calculation of $g(\omega, \{n_l^*\})$ is a good description of the force constants with respect to the rigid displacements of the substrate layers for Cu and Ni. As shown in Fig. 2, a simple one-parameter nearest

neighbor central force constant model between the atoms gives a good account of the measured dispersion of phonons propagating along the [110] direction for both Cu and Ni. [8,9] This dispersion relation shows a local maximum well within the Brillouin zone boundary in contrast to the calculated dispersion for phonons along the other two directions. This behavior is a direct consequence of the fact that an atom in a metal layer normal to the [110] direction has nearest neighboring atoms in both the first and second neighboring layers while it has only nearest neighbors in the first neighboring layers for layers normal to the [111] or the [100] directions. Thus the eigenvalue problem for the dynamics of the phonons in the [110] direction will have up to second nearest interlayer force constants ;

$$\omega^2 u_l = \frac{k}{M}(4u_l - u_{l-2} - u_{l-1} - u_{l+1} - u_{l+2}) \ . \tag{4}$$

Here the force constant k is directly related to the frequency ω_{max} by $k/M = \omega_{max}^2/8$. Note that the second nearest interlayer force constant is as strong as the first interlayer force constant. This causes the restoring force for a displacement field to be larger at the reduced wave vector $\varsigma=0.5$ than at the zone boundary $\varsigma=1.0$. For the other two directions the geometrical configuration of the atoms causes the interlayer force constants to be twice as large and to couple only to the nearest neighboring layers. This causes the restoring force to be monotonic with ς and to be larger than the corresponding forces for the [110] direction at $\varsigma=1.0$.

The loss of coordination for the atoms at the surface is the only effect taken into consideration in modelling the inter- and intralayer surface force constants. In the case of the (110) surface this gives rise to the following modification of Eq. (4) at the two outermost layers

$$\begin{cases} \omega^2 u_1 = \dfrac{k}{M}(2u_1 - u_2 - u_3) \, , \\ \omega^2 u_2 = \dfrac{k}{M}(3u_2 - u_1 - u_3 - u_4) \, . \end{cases} \tag{5}$$

All the stationary points in the dispersion relations for the phonons in Fig. 2 give rise to divergent van Hove singularities in the density of states projected on the bulk layers as shown in Fig. 3 . These divergences disappear in the projection on the surface layers, due to the destructive interference between the incident and reflected phonons from the surface at these energies. For the (110) surface, there is a pseudo band gap (c.f. Fig.3 upper panel) for $0 < \omega < \omega_{max}/\sqrt{2}$, and for every energy in this range there exists an evanescent wave localized to the surface. At a certain energy depending on the surface force constants this wave will have minimal coupling through Eq.(5) to the bulk phonons and will show up as a resonance as seen in Fig. 3. For the (111) and (100) surfaces there are no distinct spectral features in the corresponding density of states.

A detailed comparison of the calculated resonance with the experimental spectra has been done by including the frequency dependent prefactors appearing in Eqs. (1) and (4), and by integration of the inelastic scattering probability over the acceptance aperture of the detector. The resulting electron energy loss function, $I(\omega)$ (inset in Fig. 1), shows a rather sharp loss feature which agrees closely with the measured loss peak and is only 2 meV broader than the instrumental resolution. This agreement, equally good for the corresponding Cu surface, implies that the changes in the surface interlayer force constants from the bulk values are no more than $\pm 15\%$. The measured spectral loss intensities in Fig. 1 are reproduced with the effective charges $e^* = 0.024 \pm 0.003$ and 0.028 ± 0.003 for Cu and Ni, respectively, which are only slightly larger than the value 0.016 obtained for Cu atoms in the surface region [6].

In summary surface resonances of longitudinal bulk phonons have been observed on the (110) surfaces of Cu and Ni. These sharp resonances are shown to be a general feature of the (110) surface of face centered crystals with peak energies scaling with the maximum bulk phonon energies. Detailed comparison of measured spectra with results from surface lattice dynamics shows that there are no significant stiffening or softening of the surface force constants.

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Figure Captions

1. Electron energy loss spectra of clean Cu(110) (upper panel) and Ni(110) (lower panel) surfaces. The spectra were recorded at 300 K in the specular direction. Sharp spectral features are observed both on the loss and the gain side at 20 and 24 meV for Cu and Ni, respectively .The inset shows the calculated electron energy loss function $I(\omega)$ for the clean Ni(110) surface normalized to the maximum elastic intensity. The instrumental resolution is accounted for by Gaussian broadening with 4 meV at full-width-half-maximum (FWHM). The effective charges e^* and $-e^*$ of the two outermost surface layers have been adjusted to reproduce the measured spectral loss intensities.

2. Bulk phonon dispersion relations in reduced units along different major crystal directions for Cu and Ni. The calculated dispersion for longitudinal phonons propagating along the [110] direction (solid curve) are compared with measurements by inelastic neutron scattering [8,9] The experimental results have been scaled with the frequency ω_{max} where $\omega_{max}/\sqrt{2}$ is the measured frequency at the Brillouin zone boundary, $\omega_{max} = 29.7$ and 36.7 meV for Cu and Ni, respectively. The dashed curve is the calculated dispersion for the longitudinal bulk phonon along the crystal directions [100] and [111]. The distance between the crystal layers is d.

3. Projected density of states for the longitudinal phonons in Fig. 2. They have been calculated for a projection on the relative displacement of two neighboring bulk layers (upper panel) and the two outermost surface layers (lower panel). The resonance in the density of states projected on the surface layers for the phonons propagating along the [110] direction (solid curve in the lower panel) peaks at 19.4 and 24.0 meV for Cu and Ni, respectively.
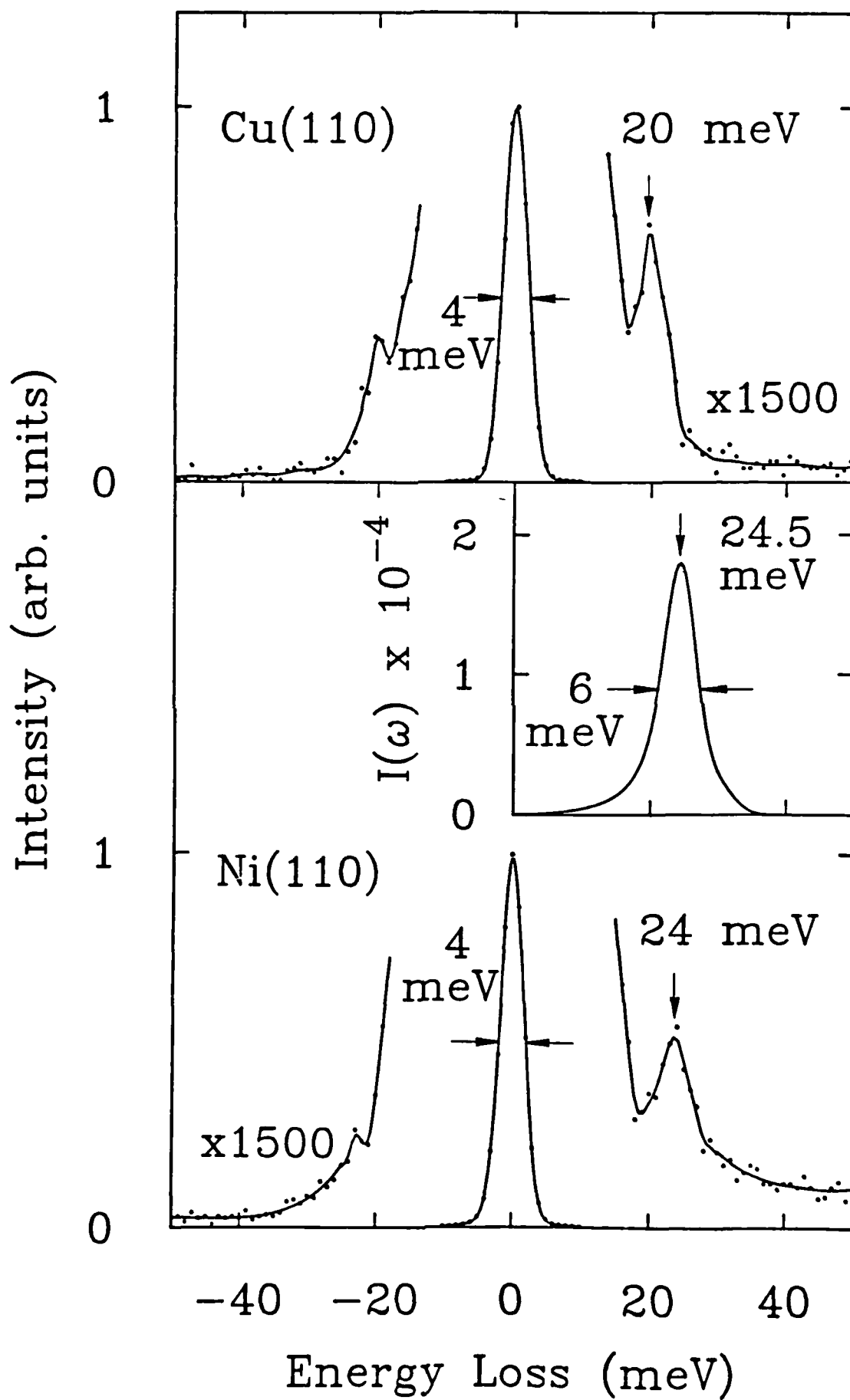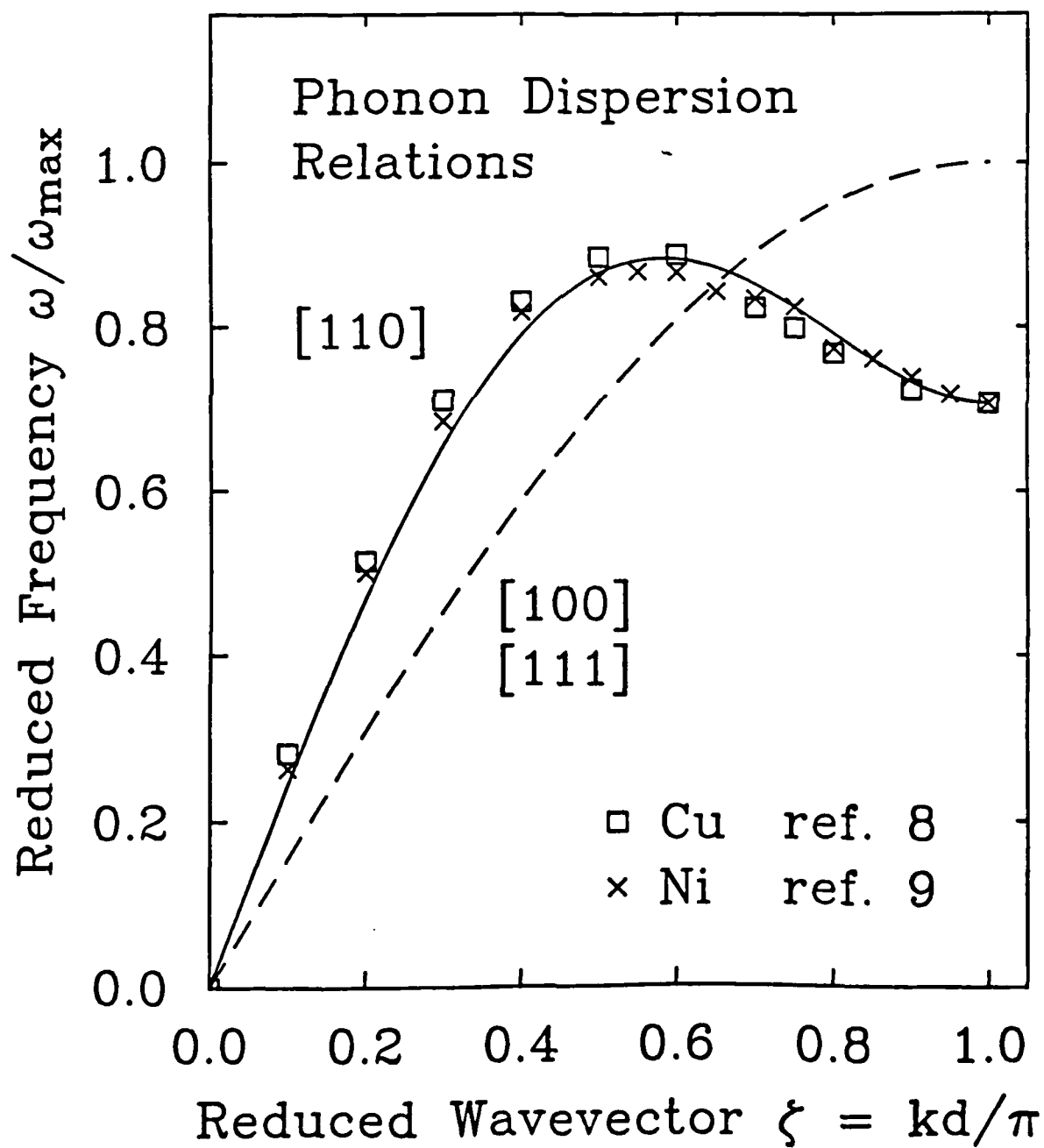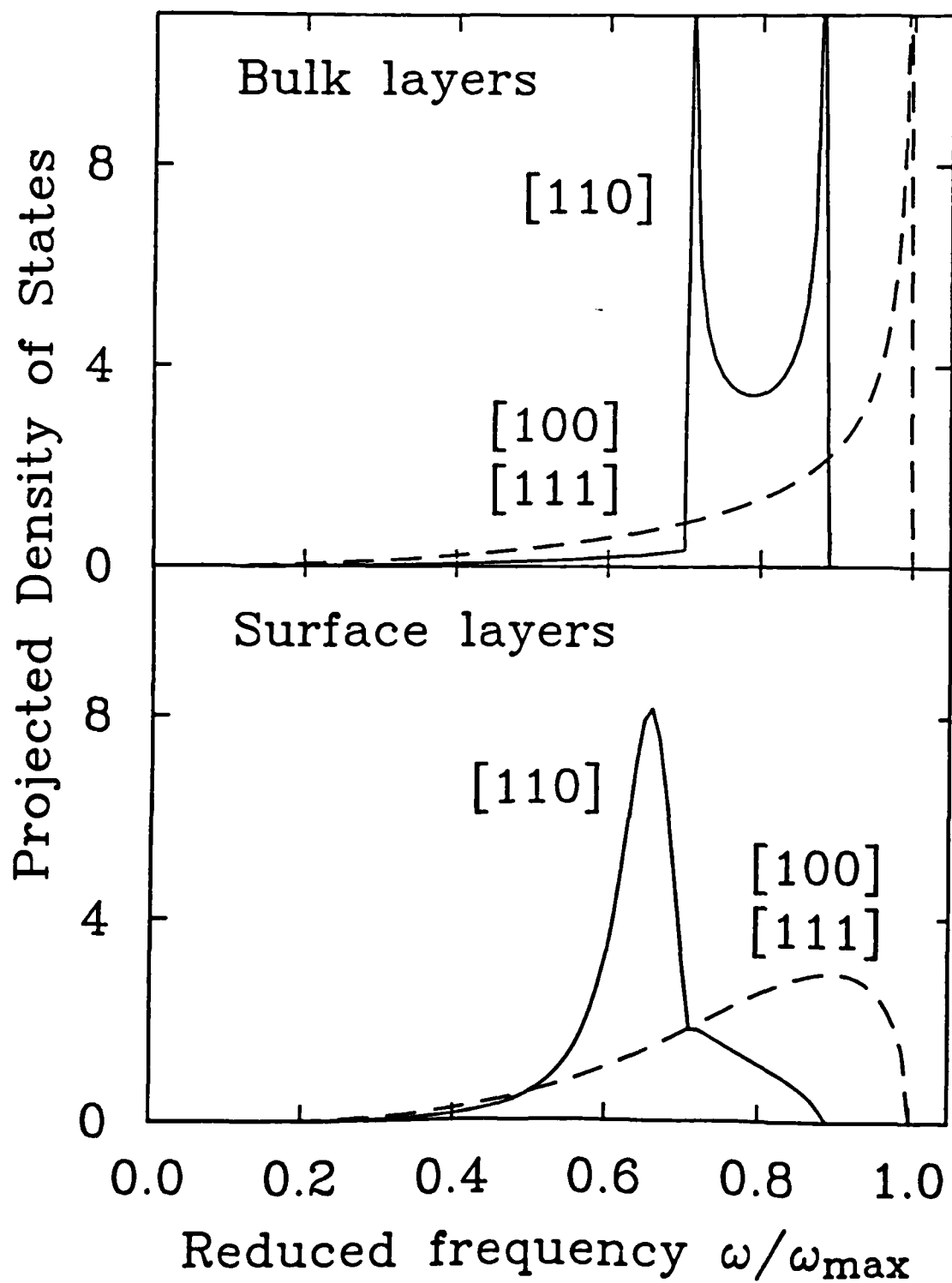
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